

## CATALYTIC UPGRADING OF BIOCRUDE OIL VAPORS TO PRODUCE HYDROCARBONS FOR OIL REFINERY APPLICATIONS

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### **BACKGROUND**

Historically, liquid transportation fuels have been processed from petroleum crude oil through a series of chemical processes in a refinery. Initially, the refinery was little more than a distillation tower that made gasoline, kerosene, fuel oils, and asphalt. Over the last 90 years, this industry has become increasingly complex as the public demanded higher octane gasolines; removing tetraethyl lead; reducing aromatics and olefins; reducing vapor pressure; adding ethers and alcohols to promote cleaner burning; and in the future, completely reformulating gasoline to burn even cleaner. As a result of these changes, refiners have already begun to look at using commodity chemicals as a significant fraction of the gasoline pool, e.g., methanol, ethanol, methyl tertiary butyl ether (MTBE), and ethyl tertiary butyl ether (ETBE). This means that refiners are already incorporating non-traditional feedstocks into the gasoline pool.

Because methanol is made through a syngas route, any form of carbon can be used to produce the syngas and therefore the methanol. Although ethanol can be made from ethylene, it is now made commercially by fermentation. These alcohols are currently purchased from the chemical industry to produce MTBE or ETBE in many oil refineries. The interest in producing MTBE within the oil refinery goes back to the reduction of gasoline vapor pressure that resulted in a surplus of butanes at the refinery. These butanes can be converted to the isobutene needed to make MTBE within the refinery in a new process step that is now being widely practiced.

It has been widely predicted that the demand for MTBE or ETBE will exceed the availability of isobutene within the refinery. Ethers made from other feedstocks are now being investigated, e.g., diisopropyl ether (DIPE) made from propene and water, as well as tertiary amyl methyl ether (TAME) made from reactive isopentenenes and methanol. However, there will be competition within the refinery for the propene and the isopentenenes to react with isobutane to make the isoparaffinic alkylates (Unzelman 1994). It appears that the time may be right for refiners to begin to consider alternative sources of olefins.

The threat of global warming, the current discussion about the capacity of the American farming industry, and the increased dependence upon oil imported from politically unstable parts of the world all combine to create an interest in alternative fuel sources. An alternative fuel source that is commonly overlooked by the petroleum industry is renewable biomass. Currently research is underway to develop agricultural crops for their energy content. Although these crops are not yet widely available for industrial use, there is a large amount of municipal solid waste (MSW) that is generated on a daily basis that would be suitable for feedstocks.

The organic fraction of the MSW is called refuse derived fuel (RDF). After drying, RDF is composed primarily of paper derived from biomass, yard wastes, polyolefinic plastics, and miscellaneous plastics. Current projections are that the paper fraction will slowly decrease while the plastic fraction will increase with time. By the year 2000, it is projected that RDF will consist of 76 wt% lignocellulosic-derived material and 24% plastics. About two-thirds of these plastics are projected to be polyolefinic. (Franklin 1994) During thermal pyrolysis, these plastics tend to depolymerize to oligomers and monomers. With catalytic cracking, the yield of monomers can be increased, similar to cracking waxes. MSW is available now in commercial quantities and the olefin yields will be higher from RDF than from a typical biomass. Because of the increasing cost of landfilling, the projected costs of the RDF are very low.

As an example, the tipping fee paid by a city to the landfill may be \$25 per ton, from which perhaps half a ton of RDF could be derived. If it were to cost \$30 to recover and prepare this RDF for use as a feedstock, it would have a net cost of \$5 for the half ton or \$10 per ton. This RDF has a heating value of about 10,000 BTU/lb that results in a cost of \$0.55/GJ, \$0.50/MMBTU, or \$2.90 per barrel of oil equivalent. This is clearly a bargain, even in today's depressed oil market. The problems with using RDF are many, but tend to be associated with the unknown minute-to-minute variability of its composition, including heavy metals, sulfur, and chlorine content.

For a variety of reasons, many oil refineries are located near large metropolitan areas along the West, East, and Gulf Coasts. Thus, these refineries are also located near potential sources of large amounts of RDF areas set aside for heavy industry, which should facilitate permitting an additional process. Also, the oil refineries typically already know how to deal with a variety of heavy metals, sulfur, and chlorine found in different crude oils. Using RDF as a feedstock in an oil refinery should pose problems of a chemical nature that are similar to those dealt with now on a day-to-day basis. However, feeding biomass and/or RDF into a refinery involves a different set of problems, which we are now addressing in our DOE sponsored Biofuels Program.

## **INTRODUCTION**

We have developed a thermal cracking or pyrolysis process in which the solid feed is metered into a vortex reactor. An extremely rapid heat transfer to the solid particles through the reactor wall results primarily in the vaporization of the lignocellulosic and thermoplastic feedstock mixtures. Byproduct char is removed from the hot vapor stream. The vapors can then be condensed to form a biocrude oil or they can be passed immediately to a catalytic cracking and deoxygenation reactor. This pyrolysis technology has been demonstrated at the 20 kg/h scale at NREL (Diebold and Scahill 1988) and is being scaled up to the 35 TPD scale by Interchem (Johnson, et al. 1993).

The biocrude oil made from lignocellulosic biomass is a fairly fluid, highly oxygenated, and polar liquid. More than 200 compounds have been identified in the biocrude, but typically at less than 5% each. However, the RDF-derived crude is a multiphase material because of the presence of polar liquids derived from the lignocellulosics and non-polar liquids and solid waxes that represent partially cracked plastics (Diebold, et al. 1989). If the pyrolysis step is integrated into an oil refinery, it is more efficient thermally to close-couple the pyrolysis step to a vapor-phase catalytic cracking step, than to condense the oil and then reheat it for further refining. Because of the highly oxygenated nature of the biocrude, it is a reactive material at elevated temperatures and does not distill well.

The challenge for the agricultural industry of the future will be to develop low cost biomass crops that have high hydrocarbon or lipid contents, which in turn would have high olefin yields in the process discussed here. In the mean time, a process that can convert RDF containing mixed plastics, paper, and yard wastes to an olefin rich stream has a niche market application that may have good economic potential. Initially using low cost RDF in this process will pave the way for the eventual use of more expensive, dedicated feedstocks produced by the agricultural industry.

This paper discusses the process of catalytically deoxygenating and cracking biocrude vapors to form hydrocarbons. The reaction of several oxygenated organic compounds over zeolite catalysts, especially ZSM-5, has been studied and reported in the literature, e.g., methanol, ethanol, acetic acid, acetone, methyl acetate, fatty acids, triglycerides, phenols, and carbohydrates. In general, the reactions that take place over ZSM-5 are those that result in forming hydrocarbons by the rejection of oxygen from the oxygenated feedstock as carbon oxides or as water. The oxygen-rejection mode is strongly dependent upon the feedstock. For example, water is rejected from methanol, carbon monoxide and water are rejected equally from propionaldehyde on a molar basis, and carbon dioxide and water are equally rejected from acetic acid on a molar basis (Chang and Silvestri, 1977) (Chen, et al., 1989).

Using the ZSM-5 catalyst (donated by Mobil) to crack the pyrolysis vapors made from biomass (Evans and Milne 1988) and from RDF (Rejai, et al 1991) has been extensively studied at NREL, using a molecular beam mass spectrometer (MBMS). With this analytical technique, the vapor effluent from a reactor containing 1 gram of catalyst can be followed in real time, with several scans per second. This allows the study of transient and steady-state products from the catalytic reactor over a range of molecular weights from near zero to several hundred.

## EXPERIMENTAL

A larger reactor containing 100 g of Mobil's extruded ZSM-5 catalyst was used to study the conversion of a 1 to 3% slipstream of pyrolysis vapors made with the vortex reactor. This reactor was fitted with an axial thermocouple well and originally with a thermocouple that could be moved axially. This single thermocouple was replaced with a bundle of 12 miniature thermocouples with a 2.54 cm axial spacing. The reactions of the biomass vapors over the ZSM-5 were mildly exothermic with temperature rises of about 20°C commonly seen. These temperature rises correspond to about 75 J/g of biomass fed or the equivalent heat release of the combustion of 0.2 g of coke per 100 g of biomass fed. The gradual decline in the catalyst activity was monitored by the movement of the exothermic temperature profile down the bed, as it "band-aged." A series of experiments at different temperatures showed quite dramatically that when steam was used as the carrier gas, the rate of band-aging was reduced at higher operating temperatures to become relatively low at 525°C. This rate of catalyst deactivation is relatively high for fixed-bed operation, but is very low for riser cracker operation. The catalyst was repeatedly regenerated by controlled air oxidation. Gas analysis was by gas chromatography (GC). The mass balance of Run 119 for the slipstream reactor system is shown in Table 1.

The fixed-bed reactor was then scaled up to be large enough to be fed the entire output of the vortex pyrolysis reactor. It has a diameter of 25 cm, a bed height 30 cm, and 7500 to 8500 g of ZSM-5 extrudate donated by Mobil. This reactor was originally fitted with an axial thermocouple well into which a bundle of 12 miniature thermocouples was placed, with an axial spacing of the thermocouples of 2.54 cm.

RDF was obtained from the MSW facility at Thief River Falls, MN, to be used as feed for the vortex pyrolysis reactor coupled to the large catalytic reactor. This RDF results after removing recyclables and non-organic materials. In Run 142, the oven dried, plastics-containing RDF was fed initially at a rate of 10 kg/h with a carrier-steam-to-RDF weight ratio of 2. The exothermic reactions appeared to take place near the entrance of the bed, with an exotherm of 15 to 20°C measured 2.5 cm into the bed. This exotherm corresponded to a heat of reaction of about 100 J/g of RDF. The feeding rate was then increased to 15 kg/h with a steam-to-RDF weight ratio of 1.3. Because of this decrease in the relative amount of steam present to absorb the heat of reaction, the temperature was seen to increase an additional 15°C. The heat of reaction was calculated to be a slightly higher value of 130 J/g of RDF for this higher feeding rate. However, the exotherm was still appearing in the first 2.5 cm of the 30 cm bed. The rest of the bed exhibited a slight cooling and then a slight exotherm near the outlet of the bed. We speculate that three sequential global reactions could be taking place that would have a net exothermic, endothermic, and finally exothermic effect. However, the temperature measuring arrangement was subject to apparent conductive errors that were progressively more severe in the last 7.5 cm of the reactor. These errors were because of a combination of poor convective heat transfer from the axially flowing gases and heat conduction and radiation to the cooler exit flange of the reactor (which was massive and difficult to heat). Gas analysis was by GC. The yields from this run are shown in Table 1. We think that the plastics content of the RDF contributes to the relatively higher yields of olefins.

This reactor was later modified by adding 12 gas sampling tubes at 2.54 cm intervals along the reactor length. Each sampling tube penetrated two-thirds across the reactor diameter. Projecting a millimeter past the entrance of the sampling tube was a thermocouple to measure the local temperature, with the thermocouple serving to reduce the volume of the sampling port. The sample ports were angularly spaced in a helical fashion to minimize their interaction. With the thermocouples heated directly by cross-flowing gases at 15 cm from the reactor wall, the conduction errors were greatly reduced. In addition, three thermowells were installed on diameters to allow the diametrical temperature gradient to be followed with a bundle of eight miniature thermocouples spaced 2.54 cm apart. With just carrier gas passing through this large fixed-bed reactor and with thermocouples from one manufacturer's lot, the helically spaced thermocouples showed that an isothermal bed could be maintained to within  $\pm 1^\circ\text{C}$ . With this reactor, the progress of the conversion of the pyrolysis vapors as a function of the amount of catalyst encountered could be monitored by temperature measurements and gas samples. Thus, 12 different space velocities could be evaluated in a single experiment. Each sample port was fitted with an evacuated sample bottle so that the samples could be taken manually at essentially the same time in the run.

An example of using the modified large fixed-bed reactor was Run 144. This run used oven-dried Southern Pine sawdust at a feeding rate of 15 kg/h. The steam-to-biomass weight ratio was 1.33. The weight hourly space velocity varied from 19 at the first sampling port to 1.6 at the twelfth sampling port. The initial bed temperature prior to the start of feeding the sawdust was 520°C. The temperature profile through the bed was different than had been measured for the smaller 100-g reactor using an axial thermowell. The temperature profile in this run with wood showed a steady

increase in temperature over the length of the bed. This is indicative of exothermic reactions occurring throughout the bed. The initial temperature rise was 91°C and gradually decreased to 46°C after two hours of operation. These increases in temperature corresponded to exothermic reactions on the fresh catalyst of about 350 J/g of wood fed and on the partially deactivated catalyst of about 175 J/g after two hours on stream. It has been reported that with methanol as feed, ZSM-5 has an initially high rate of coke formation, followed by a long period of a lower rate of coke formation, while slowly losing activity (Bibby, et al. 1986). GC analysis of gas samples taken 43 minutes into the run showed that most of the methane, carbon monoxide, and carbon dioxide were formed in the first 3 cm of the 30 cm long bed. At 113 minutes into the run, the catalyst showed some deactivation and these permanent gases were produced in the first 10 cm of the bed. The olefin yields were shown to steadily increase throughout the bed, but the overall olefin yield appeared to decrease as the experiment progressed. The overall olefin yields were about 5 to 6 wt% of the wood fed. We speculated that the initially observed high heat of reaction corresponds to an initially high rate of coke deposition on the catalyst, as well as to a lowered activity with time toward the more refractory compounds in the vapor stream.

## **DISCUSSION AND CONCLUSIONS**

The limited operation of the 100 and the 8500 g fixed-bed reactors demonstrated general agreement with operating the 1 g reactor used in the MBMS experiments. Operating the larger reactors is not considered to have been sufficient to optimize the yields. However, we demonstrated that the overall reactions of the RDF and the wood vapors over ZSM-5 catalyst are slightly exothermic in nature, which was not observable with the 1 g reactor. The largest reactor appeared to be more adiabatic to result in higher temperatures from the reactions. The heat of reaction appears to be about 175 to 350 J/g of wood and 100 to 135 J/g of RDF. Much of the variation in the calculated heat of reaction is thought to be because of different products being made by the catalyst at different activity levels.

These heats of reaction are relatively small and correspond to the heat that would be released by the combustion of less than about 1 g of coke per 100 g of feed. However, the exothermic reactions have a very large impact on the design of a riser cracker. In the cracking of petroleum in an FCC refinery unit, the overall reactions are quite endothermic. This heat requirement is met by burning off some coke from the catalyst after each time the catalyst passes through the catalytic riser cracker in the FCC unit. This balance of heat around the FCC unit poses operational requirements, which dictates the rate of catalyst circulation and reduces the amount of heat that can be recovered from the catalyst regenerator. With an exothermic reaction taking place in the case of cracking pyrolysis vapors, the rate of catalyst circulation is dictated only by the chemistry involved, not a tradeoff of the chemistry against the energy balance.

With a fixed-bed reactor, there must be extra catalyst present to allow for some catalyst deactivation to occur prior to taking the bed out of service for regeneration. If the purpose of the reactor is to take the products toward thermodynamic equilibrium, there is no loss in the intended products by exposure to the added catalyst. However, at the high temperatures we must operate to minimize coke formation, any olefins initially formed are being rapidly converted irreversibly to aromatics (Chen, et al. 1989). Thus, if the preferred products are olefins for manufacturing reformulated gasolines, rather than aromatics, it is desirable to have just enough catalyst present to prevent breakthrough of the unwanted pyrolysis materials. In a riser cracker, this can be easily accomplished by simply adjusting the relative rate of catalyst circulated to the feeding rate. The non-steady state operation of a fixed-bed reactor undergoing rapid catalyst deactivation would tend to upset any downstream processing. For these and other reasons, the petroleum refining industry moved from fixed-bed to fluidized-bed catalytic cracking (FCC) about 50 years ago, which in turn evolved into the riser cracker about 40 years ago. The results of the larger fixed-bed reactors presented here were relatively preliminary, but they were used to confirm the conclusion that the preferred cracking reactor for pyrolysis vapors would be a more complex riser cracker.

We have constructed a catalytic riser cracker matched to the output of the vortex pyrolysis reactor. We currently are in the final stages of shakedown and expect to be generating experimental data very shortly. We will be evaluating the use of different feedstocks, e.g., wood, a uniform plastic-coated paper, real RDF, and a biomass naturally containing large amounts of oils or waxes for producing hydrocarbons of interest to petroleum refineries.

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Table 1. Yields from Upgrading Pyrolysis vapors with Mobil's ZSM-5 catalyst

	<u>Run 119</u>	<u>Run 142</u>
Feed	So. Pine	RDF
Catalyst bed size, g	100	7500
H <sub>2</sub> , wt % of dry feed	0.1	0.3
CO	15.4	20.8
CO <sub>2</sub>	8.1	16.7
CH <sub>4</sub>	1.1	1.9
C <sub>2</sub> -C <sub>4</sub>	3.6*	10.7*
C <sub>5</sub> + gasoline	8.8	4.9
Fuel Oil	13.2	4.3
Pyrolysis Char	15.1	19.8
Coke on catalyst	9.4	6.8
H <sub>2</sub> O (by difference)	25.2	13.8
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	100.0	100.0

\* 94 wt% olefins